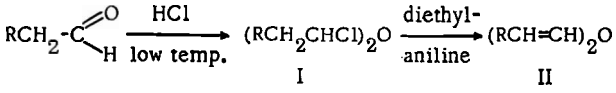
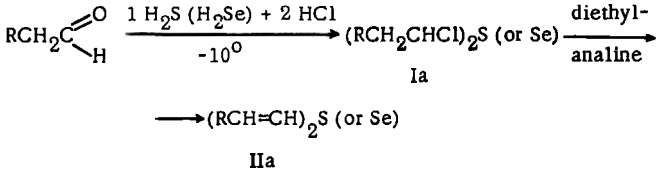
SUMMARY

In this thesis the preparation of some new types of unsaturated ethers, thioethers and selenoethers is described.

Chapter I deals with the preparation of di(alk-1-enyl)ethers, -thioethers and -selenoethers RCH=CH-X-CH=CHR (X is O, S or Se, R is H or alkyl). The oxygen-ethers were obtainable in a simple manner, starting from aliphatic aldehydes. The latter compounds were first converted into 1,1-dichlorodialkyl ethers (I) by means of anhydrous hydrogen chloride; the dichloroethers in turn were heated with diethylaniline, which produced the di(alk-1-enyl)ethers (II):

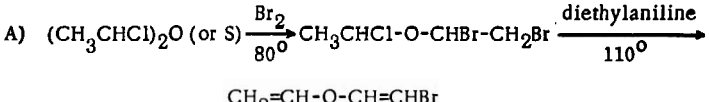


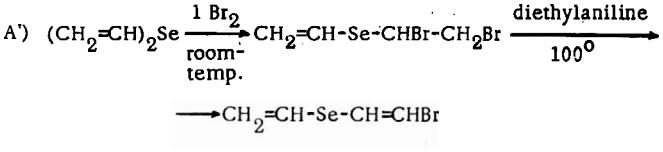
The analogous thioethers and selenoethers (IIa) were prepared by heating 1,1'-dichlorodialkylthioethers or -selenoethers (Ia) with diethylaniline. The latter compounds were accessible by passing a mixture of gasuous HCl and H_2S or H_2Se in the mol. proportion 2 : 1 into aldehydes:

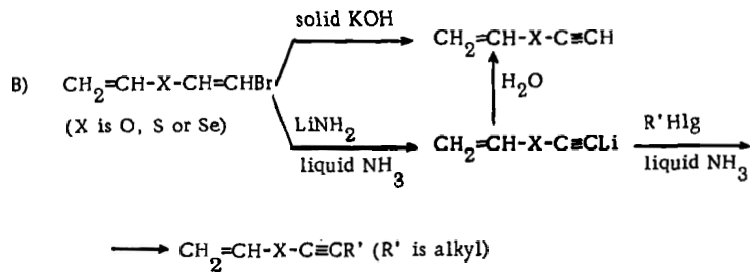


The overall yields were reasonable.

In chapter II the synthesis of compounds, containing the system -C≡C-X-CH≡C< (X is O, S or Se) is described. The synthetic routes are apparent from the reaction schemes A-C:







With the higher 1,1'-dichlorodialkylethers and -thioethers $(RCH_2CHCl)_2O$ (or S) scheme A led to the compounds RCBr=CH-O-CH=CHR (or S) (with R is CH_3, C_2H_5, ...), which could be dehydrobrominated to the alkenyloxy- or alkenylthio--1-alkynes RC≡C-O-CH=CHR (or S):

$$RCBr{=}CH{-}O{-}CH{=}CHR \xrightarrow[\text{or } LiNH_2/\text{liquid } NH_3]{KOH} RC{\equiv}C{-}O{-}CH{=}CHR \text{ (or S)}$$

C) $(RCH_2CH_2)_2S_2 \xrightarrow[-20^\circ]{SO_2Cl_2} RCH_2CHCl{-}SCl \xrightarrow{R''C{\equiv}CH} R''CCl{=}CH{-}S{-}CHClCH_2R$

$$\xrightarrow[115\text{-}120^\circ]{\text{diethylaniline}} R''CCl{=}CH{-}S{-}CH{=}CHR \xrightarrow[\text{liquid } NH_3]{NaNH_2} R''C{\equiv}C{-}S{-}CH{=}CHR$$

(R" and R=H or alkyl)

Scheme C represents a method to prepare the alkenylthio-1-alkynes on a larger scale.

Chapter III is devoted to the synthesis of di(alk-1-ynyl)ethers and -thioethers RC≡C-X-C≡CR.
The unstable diethynylthioether $(HC{\equiv}C)_2S$, and its derivatives were obtained in the following ways:

1) $RC{\equiv}CH \xrightarrow{SCl_2} (RCCl{=}CH)_2S \xrightarrow[\text{liquid } NH_3]{2\ LiNH_2} (RC{\equiv}C)_2S$

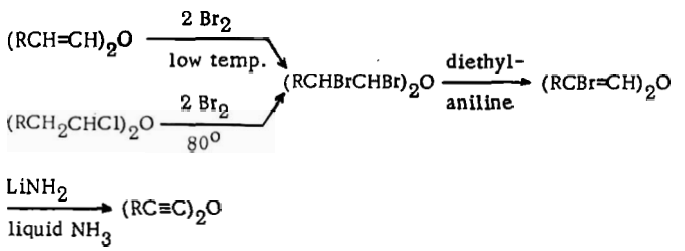
2) $(CH_2{=}CH)_2S \xrightarrow{2\ Br_2} (CH_2BrCHBr)_2S \xrightarrow[120^\circ]{\text{diethylaniline}}$

$$(CHBr{=}CH)_2S \xrightarrow[\text{liquid } NH_3]{4\ NaNH_2\ (+\ \text{excess})} (NaC{\equiv}C)_2S \begin{cases} \xrightarrow{H_2O} (HC{\equiv}C)_2S \quad \text{III} \\ \xrightarrow[\text{liquid } NH_3]{RBr} (RC{\equiv}C)_2S \quad \text{IV} \end{cases}$$

In the first scheme sulfur dichloride is added to an 1-alkyne; the adduct furnishes the di(alk-1-ynyl)thioethers, on treating with two equivalents of $LiNH_2$ in liquid ammonia.

In the second scheme 2, 2'-dibromodivinylthioether (obtained from divinylthioether) is converted into the disodio-compound of diethynylthioether, which can be alkylated to the dialkynyl-thioethers (IV) or hydrolyzed to diethynylthioether (III).

The formation of the extremely unstable dialkynylethers $(RC{\equiv}C)_2O$ of which only dipropynylether $(CH_3C{\equiv}C)_2O$ has been isolated, proceeded as follows:



The first representative $(HC{\equiv}C)_2O$ seemed to be unstable even at -70°.